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Experimental investigations on the phase equilibrium of semiclathrate hydrates of carbon dioxide in TBAB with small amount of surfactant

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Abstract

Experimental studies are carried out on a semiclathrate hydrate system of carbon dioxide in tetra-*n*-butyl-ammonium bromide (TBAB) with a small amount of surfactant, sodium dodecyl sulfate (SDS), for 5, 10, and 20 wt.% TBAB to determine the phase equilibrium temperature and pressure conditions. It is observed that the presence of SDS did not influence the equilibrium conditions of the semiclathrate hydrate. Re-nucleation (memory) effect of semiclathrate hydrates of CO_2 is studied for few cases of TBAB concentration in an aqueous solution. The equilibrium pressure and temperature conditions obtained for memory effect and regular experimental run without memory effect were observed to be quite close. It is concluded that in the case of no memory effect, with increasing TBAB percentage in the system, the time required for nucleation is reduced. For the same TBAB concentration, the incipient pressure and temperature required for nucleation and re-nucleation of semiclathrate hydrates increase while the time required for re-nucleation decreases.

Keywords: Carbon dioxide, Clathrate hydrate, Phase equilibria, Semiclathrate hydrate, Surfactant

Background

Global warming of the Earth's atmosphere has increased concerns for the conservation of Mother Nature. The melting of glaciers, the encroaching sea line on the coastal areas, decreasing agricultural outputs, health effects on human beings are considered to be some of the major effects of this phenomenon. The burning of fossil fuels and even the use of renewable energies have drastically increased carbon dioxide (CO_2) emission in the atmosphere. It is, therefore, important to look at the proper disposal of carbon dioxide so as to reduce post-use implications of fossil fuels. Carbon capture and sequestration (CCS) is considered to be one of the prime remedy for global warming. However, it is more expensive and technically challenging to have CCS performed in the formation. Additionally, CO_2 leakage from reservoirs may pose a risk to overlying fresh groundwater and also may suddenly increase CO_2 percentage in subsurface environments affecting the marine life [1-3]. In order to mitigate CO_2 leakage and make it more stable in the reservoirs, several methods are being investigated. One of the proposed methods of CO_2 sequestration is using it in the form of gas hydrate and injecting them into the reservoir [4,5]. Additionally, CO_2 can be transported in the form of gas hydrate slurries. However, more efforts have to be made to make the process more economical and safe.

Gas hydrates, also referred to as clathrate hydrates, form under extreme conditions of low temperature (typically <10°C) and high pressure (typically >3 MPa), when gases (guest) like carbon dioxide, methane, nitrogen, come in contact with water (host) [6]. Precise conditions in terms of pressure and temperature depend on the composition of the guest gas. These hydrates get destroyed by destabilizing the phase equilibrium condition, typically by raising the temperature or decreasing the pressure or by employing chemical inhibitors. Semiclathrate hydrates are similar to gas hydrates but have a different lattice structure. This structural difference arises because semiclathrate hydrates are formed when the gas hydrate system contains some thermodynamic promoter, such as tetra-*n*-butyl-ammonium

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bromide (TBAB), tetra-*n*-butyl-ammonium chloride, tetra-*n*-butyl-ammonium fluoride. TBAB in water forms a semiclathrate hydrate which shares similar physical and structural properties as true clathrate hydrates. The principal difference is that, unlike true clathrates where the guest molecules are not physically bonded within the water structure, in semiclathrate hydrates, the host/guest molecules of TBAB may form the part of the water lattice (host) as well as occupy cages (guest) along with the gas molecules [7-10]. Typically, semiclathrate hydrates are formed at lower conditions of pressure and temperature as compared with the gas hydrate system for the same gas as a guest molecule. Typically, in the semiclathrate structure of TBAB, one TBAB and 38 H_2O molecules form a hydrate structure. Semiclathrate hydrates have a wide range of engineering applications such as carbon dioxide sequestration, transportation and storage of natural gas, and flue gas separation [11-15]. Understating the phase behavior of these hydrate systems forms a precursor for their successful applications.

Arjmandi et al. [7] conducted experiments to determine the equilibrium temperature and pressure of semiclathrate hydrates of methane, carbon dioxide, and nitrogen with varying percentages of TBAB in the aqueous system. The TBAB weight percentage (wt.%) used in this study was in the range of 5 to 42.7 wt.%. A shift in the equilibrium curve of semiclathrate hydrates to the right as compared with that for pure clathrate hydrate systems is observed. This shift implies that semiclathrate hydrates are one of the potential 'thermodynamic' promoters of hydrate formation. The thermodynamic promoter changes the Gibbs energy of hydrate formation which shows implications for the stability condition of hydrates at complex reservoir conditions. Here, the stability of hydrate refers to the equality of fugacity of the hydrate phase and the gas phase. Kinetic promoters also refer to the catalyst which does not affect the phase equilibrium. However, the thermodynamic promoter does affect the phase equilibrium. Several researchers [11-20] conducted experiments to determine the equilibrium conditions of semiclathrate hydrate systems. Duc et al. [11] conducted phase stability experiments on carbon dioxide semiclathrate hydrates for varying TBAB weight percentages from 4.95 to 65 wt.%. Lin et al. [12] studied the phase equilibrium and dissociation enthalpy of carbon dioxide semiclathrate hydrates formed in the presence of TBAB. Sakamoto et al. [13] studied the thermodynamic behavior of hydrogen semiclathrate hydrates formed in an aqueous solution of TBAB. Li et al. [14] conducted experiments for semiclathrate hydrates of carbon dioxide for 5 and 10 wt.% TBAB. Sun et al. [15] determined equilibrium conditions of methane hydrates for 5 to 45 wt.% TBAB in the system. Li et al. [16] and Ding et al. [17] performed experiments to study the formation and dissociation of methane semiclathrate hydrates in an aqueous system containing TBAB. Mohammadi et al. [18,19] conducted experiments to determine the phase behavior of an aqueous system of methane, hydrogen sulfide, carbon dioxide, and nitrogen in the presence of TBAB. Ye and Zhang [20] studied the phase equilibrium of CO_2 in TBAB aqueous solution. The effect of the kinetic promoter (surfactant) such as sodium dodecyl sulfate (SDS) is observed to increase the formation of clathrate hydrates of methane while not affecting the phase equilibria [21]. The use of SDS (kinetic promoter) along with TBAB (thermodynamic promoter) may help to increase the efficiency of the system, making it more useful for CO_2 sequestration and gas storage and transportation. However, the phase behavior of CO_2 hydrates containing both agents is not reported and needs more investigation.

Memory effect has been studied in the crystallization of clathrate hydrates [22]. It is a phenomenon in which the re-nucleation of hydrate crystals occurs at a lower pressure of at least 1 MPa and a higher temperature of at least 2 K than the initial nucleation of hydrates. Parent and Bishnoi [23] conducted experiments to study the memory effect of methane + water system. Takeya et al. [24] performed experiments to analyze memory effect of carbon dioxide + water system. Ohmura et al. [25] observed that the re-nucleation probability and induction time depend on the temperature after the dissociation of initial gas hydrate. Oshima et al. [26] found that the re-nucleation phenomena of semiclathrate hydrates occurred at conditions of temperature 1 K higher than the nucleation temperature of the initial semiclathrate hydrate. It is observed that the effect of the concentration of TBAB on incipient pressure, temperature, and time required for re-nucleation of semiclathrate hydrates has not yet been examined and thus requires investigation.

In this work, an experimental study is performed on the phase behavior of semiclathrate hydrates of carbon dioxide in TBAB aqueous solution with a small amount of surfactant, SDS, for varying weight percentages of TBAB to understand the effect of SDS on the phase stability of the system. Re-nucleation (memory) effect is examined for semiclathrate hydrates of carbon dioxide, and the effect of TBAB concentration on incipient conditions (pressure, temperature, and time) required for re-nucleation is discussed. The results obtained on the phase stability of the combination of CO_2 + TBAB + SDS + H_2O are new and not reported in the literature.

Methods

A detailed description about the experimental setup is given, followed by discussion on the experimental procedures.

Experimental setup

The heart of the experimental setup is a high-pressure reactor shown in Figure 1. The volume of the high-pressure reactor is 1 L. The maximum operating pressure of the reactor is 10 MPa. The reactor has a magnetic stirrer which has a maximum rotation speed of 1,000 rpm. The high-pressure reactor is installed with pressure transducers and temperature sensor, Pt-100. The reactor also has a jacket within which ethylene glycol + water solution is circulated from the Julabo® (Julabo Gmbh, Seelbach, Germany) water bath at a desired temperature of about 263.15 K (±1 K). The reactor and the Julabo® water bath is connected to a personal computer (PC; Intel® Core i5, 2 GB RAM; Intel Corporation, Santa Clara, CA, USA) and operated online. The data on pressure and temperature as a function of time are acquired at an interval 30 s and stored in the PC.

TBAB (in powder form) and SDS used in this work are of ultrapure quality and supplied by Sisco Research Laboratory Private Limited (Mumbai, India). Deionized water obtained from the Millipore® (EMD Millipore, Billerica, MA, USA) deionized setup is used to make the TBAB solution of varying weight percentages as per the requirement. Carbon dioxide gas used in this work is 99.5% pure and is supplied by Bhuruka Gas Agency (Banglore, India). The carbon dioxide cylinder is equipped with a heater at the outlet which helps the smooth flowing of gas to the reactor at the desired pressure.

Experimental procedure

Typically, two methods, the 'isochoric' and the 'isobaric' methods, are used for the determination of phase equilibrium of semiclathrate hydrates [27-31]. In this work, the isochoric method is used. The temperature of the system is reduced, which results in the reduction of the system pressure. An abrupt fall in the pressure of the system is observed at the onset of hydrate nucleation. After attaining sufficient pressure drop, the system is heated slowly until it attains initial pressure condition. The point of equilibrium is decided when the intersection of tangent is drawn between the heating and cooling lines. The isochoric method is much simpler to conduct and is relatively more accurate as compared to other methods [27,28].

An aqueous solution of a desired TBAB weight percentage with 0.1 g (0.025 wt.%) of SDS is filled in to the reactor. Carbon dioxide is purged in to the reactor to a pressure of 0.1 to 0.2 MPa for a couple of times to remove dissolved air from the aqueous TBAB solution. The reactor is then pressurized using carbon dioxide and left overnight to allow the system to become stable [31]. The reactor system is then stirred at 480 to 500 rpm and cooled to a lower temperature of about 263.15 K using the Julabo® water bath to form semiclathrate hydrates. As the semiclathrate hydrate forms, the pressure of the reactor falls rapidly. The temperature of the system is then gradually increased at the rate of 2 K/h, followed by an increase at the rate of 0.2 K/h. It is to be noted here that, with the help of several exploratory run *a priori*, we observed a slow heating rate of 0.2 K/h of the reaction mass, which was suitable for our *well-stirred* reactor system to get a *reliable* equilibrium point. To study the re-nucleation phenomena, the system is heated slightly (roughly 0.5 K) above the equilibrium temperature. This was done to ensure that all the

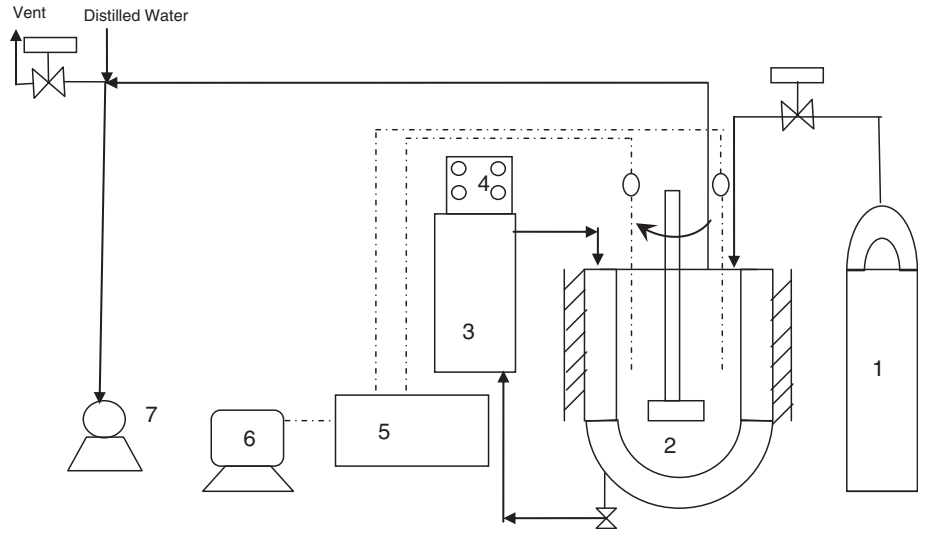

Figure 1 Details of the experimental setup used in this work. (1) CO_2 gas cylinder, (2) high-pressure reactor, (3) Julabo® water bath, (4) temperature control panel, (5) temperature and pressure data acquisition unit, (6) computer, and (7) vacuum pump.

gas from the liquid phase in the system has completely escaped to the gas phase. The reactor is then re-cooled to re-form (re-nucleate) the semiclathrate hydrates. Once a semiclathrate hydrate formation is confirmed by sudden drop in the system pressure, the temperature is raised at a rate of 2 K/h followed by 0.2 K/h until the equilibrium point is reached.

Results and discussion

In this work, an experimental study is performed on the phase behavior of semiclathrate hydrates of carbon dioxide in TBAB aqueous solution with a small amount of surfactant for varying weight percentages of TBAB. To verify the experimental procedures, experimental investigations were carried out on the pure CO_2 hydrate system for various pressure and temperature conditions to get the phase equilibrium points, followed by studies on semiclathrate hydrates of CO_2 in 5 wt.% TBAB in aqueous solution (without SDS). Figure 1 shows the results obtained for two cases along with literature data. The equilibrium data obtained for the pure CO_2 hydrate system is well matched with those in the literature. A similar behavior is observed for semiclathrate hydrates of CO_2 in 5 wt.% TBAB aqueous solution, confirming the experimental procedures. As the experimental procedure is verified, several experimental runs were performed to accumulate data sets on equilibrium pressure and temperature conditions of CO_2 semiclathrate hydrate in TBAB aqueous solution with a small amount of SDS for 5, 10, and 20 wt.% TBAB. Table 1 gives the details of experiments performed in this study.

Results on phase stability

An isochor is defined as the variation of the system pressure with temperature while keeping the volume constant. Each data point on equilibrium temperature and pressure for each TBAB weight percent (as in Table 1) generates separate isochors. A sample isochor is presented in Figure 2 for the experimental run of 20 wt.% TBAB in aqueous solution. The aqueous solution of 20 wt.% TBAB containing 0.025 wt.% SDS and the CO_2 gas in the reactor, at an initial pressure condition as shown by point A (see Figure 2), is cooled at a fast rate (−10 K/h) using cold water from the Julabo® water bath circulated through the jacket of the stirred reactor. Point

Table 1 Details of the experiments performed in this study

System	TBAB (wt.%)	Data points on equilibriums *P* and *T*
CO_2 + TBAB + H_2O	5	6
CO_2 + TBAB + H_2O	10	5
CO_2 + TBAB + H_2O	20	7

SDS weight percentage used in all experimental runs is 0.025 wt.%.

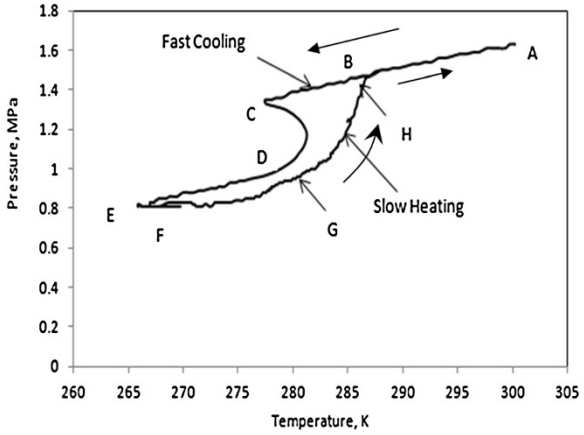

Figure 2 Typical isochor of CO_2 semiclathrate hydrate (for 20 wt.% TBAB in aqueous solution).

C represents the onset of nucleation where the system pressure is observed to decrease rapidly, deviating from the normal cooling behavior. Since semiclathrate hydrate formation is an exothermic process, an increase in temperature is observed from points C to D. The cooling is continued until point E, after which the system is heated at the rate of 2 K/h until point G, followed by a rate of 0.2 K/h until the end of the experimental run. At the end of the slow heating process, it is observed that the system retraces its path at point H. The system follows the initial path, B to A, beyond point H. The equilibrium point is decided by the intersection of tangents drawn on the heating

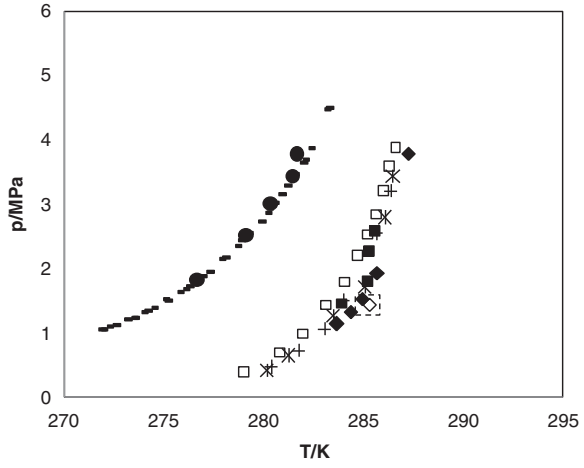

Figure 3 Experimental results for CO_2 hydrate and semiclathrate hydrates with 5 wt.% TBAB. Pure CO_2 hydrate: (black circle) this work and (small black square) Sloan and Koh [6]. Semiclathrate hydrate with 5 wt.% TBAB: (black square) this work; (asterisk) Li et al. [14]; (plus sign) Mohammadi et al. [19]; and (white square) Ye and Zhang [20]. Semiclathrate hydrate with 5 wt.% TBAB + SDS: (black diamond) this work and (white diamond) this work with memory effect.

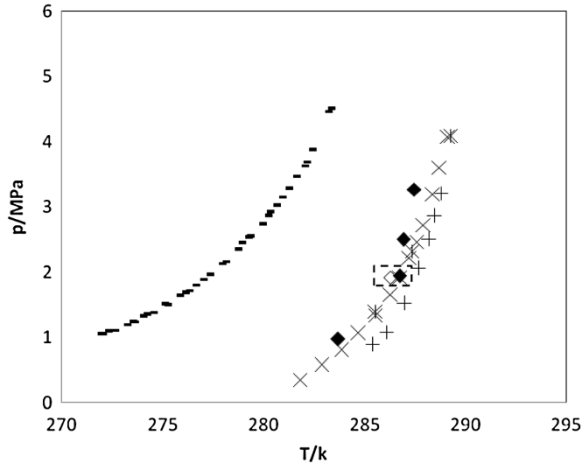

Figure 4 Experimental results for carbon dioxide hydrate and semiclathrate hydrates with 10 wt.% TBAB. Pure CO_2 hydrate: (small black square) Sloan and Koh [6]. Semiclathrate hydrate with 10 wt.% TBAB: (asterisk) Arjmandi et al. [7]; (plus sign) Mohammadi et al. [19]; and (cross sign) Ye and Zhang [20]. Semiclathrate hydrate with 10 wt.% TBAB + SDS: (black diamond) this work and (white diamond) this work with memory effect.

line and cooling line near point H as followed by other researchers [27-30]. It is to be noted here that the heating observed under semiclathrate formation can be used to determine heat of formation along with better analytical techniques, such as calorimetry or differential thermal analysis [12,32,33]; however, this measurement does not form the focus of this work.

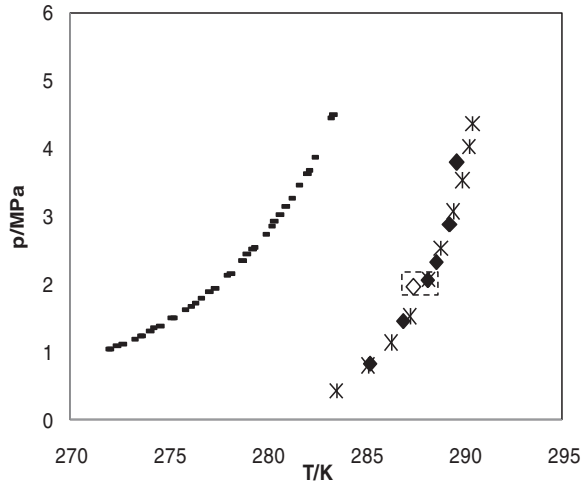

Figure 5 Experimental results for carbon dioxide hydrate and semiclathrate hydrates with 20 wt.% TBAB. Pure CO_2 hydrate: (small black square) Sloan and Koh [6]. Semiclathrate hydrate with 19 wt.% TBAB: (asterisk) Ye and Zhang [20]. Semiclathrate hydrate with 20 wt.% TBAB + SDS: (black diamond) this work and (white diamond) this work with memory effect.

Figures 3, 4 and 5 show the experimental data on phase equilibrium for the carbon dioxide semiclathrate hydrate system with 5, 10, and 20 wt.% TBAB with SDS (0.025 wt.%) in aqueous solution, respectively. The equilibrium data obtained in this work is compared with the equilibrium data available in an open literature [7,11-20]. It is found that the data obtained in this work match satisfactorily with the available equilibrium data from the literature for 5 and 10 wt.% TBAB in the system. As mentioned, we have performed experiments with an addition of 0.025 wt.% SDS in TBAB aqueous solution. The obtained results from this work show that the presence of SDS in the system does not influence the phase equilibrium of semiclathrate hydrates of carbon dioxide. The observed results are in accordance with the clathrate hydrate system of methane in the presence of a small amount of SDS [21]. SDS typically helps to increase the rate of formation of the clathrate hydrate system without affecting the equilibrium conditions, so it is termed as 'kinetic' promoters [21]. It is to be noted here that the focus of the present study is to check the effect of the presence of a surfactant on the phase equilibrium of semiclathrate hydrate system. The observed phase equilibrium data points in this study are tabulated in the Table 2.

Table 2 Equilibrium data for various TBAB percentages for semiclathrate hydrates of CO_2

TBAB (wt.%)	Equilibrium temperature (K)	Equilibrium pressure (MPa)
5	285.25	0.84
	286.90	1.47
	287.47	1.96
	288.18	2.07
	288.60	2.33
	289.29	2.89
10	283.68	0.97
	285.79	1.92
	286.73	1.94
	286.93	2.49
	287.46	3.27
20	285.25	0.87
	286.90	1.52
	287.47	2.03
	288.19	2.14
	288.60	2.41
	289.29	2.98
	289.66	3.91

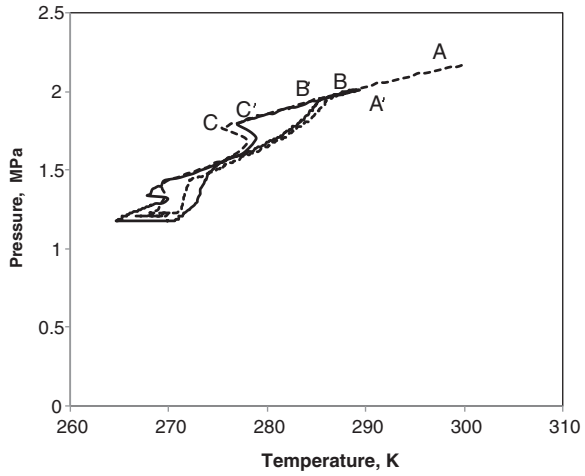

Figure 6 Re-nucleation (memory) effect for semiclathrate hydrates of CO_2 for sample case of 20 wt.% TBAB. Isochor for first run (dashed lines); isochors for memory effect (solid line). The notations on points A, B, and C are the same as those in Figure 2. A′, B′, and C′ represent experimental points for re-nucleation.

Re-nucleation effect in semiclathrate hydrate

The purpose of this study is to get an inference of the effect of the presence of TBAB concentration on the re-nucleation effect in the semiclathrate hydrate system, not to analyze the re-nucleation effect in detail. To understand the memory effect in detail, one may require more sophisticated analytical/visual techniques. A sample isochor for the re-nucleation effect for semiclathrate hydrate of CO_2 is shown in Figure 6 for a case of 20 wt.% TBAB in the system. It is to be noted that the isochor here (Figure 6) is separate from the isochor presented in Figure 2, which is representing another equilibrium point. The isochor with dashed lines in Figure 6 is for initial experimental runs (without memory effect) while the solid line represents the re-nucleation (memory effect) run. The notations for points A, B, and C are the same as those in Figure 2. A′, B′, and C′ represent the points for experimental run with re-nucleation effect. It is to be noted that the formation of semiclathrate hydrate is achieved first and then is dissociated to reach up to equilibrium point B as in Figure 6. After reaching point B, the system temperature is raised by about 0.5 K to ensure that all gas molecules from semiclathrate hydrate crystals have escaped to the bulk gas phase. This is validated by the fact that the P to T line traces back to its original cooling curve after point B (path B to A). This is then followed by re-cooling of the system to form the semiclathrate hydrates again. An analysis is done to see an effect of the TBAB concentration on nucleation condition from several cases of TBAB concentrations studied in this work. For this, out of several experimental runs (as in Table 1), three cases, one each from 5, 10, and 20 wt.% TBAB concentrations, are considered. In order to draw realistic and practical conclusions and inferences, the same initial conditions of system pressure and temperature are considered for the three cases. The three cases, thus, considered for this examination have initial conditions (point A in Figure 6) of system pressure and temperature that are nearly same. This is around 2.25 MPa of initial system pressure and nearly in the range 298.15 to 300.15 K of initial temperature. Table 3 gives a comparative study between the difference in insipient temperature and pressure conditions at which nucleation starts (point C in Figure 6) in the case of the first run and a run with memory effect (second experimental run) along with the corresponding time of re-nucleation of the semiclathrate hydrates in the system for 5, 10 and 20 wt.% TBAB. The equilibrium point obtained for memory effect and the regular experimental run are observed to be quite close (also shown in Figures 3, 4 and 5). It is observed from Table 3 that for the case of no memory effect with increase in TBAB percentage in the system, the time required for nucleation reduces and so is for the case of memory effect. Additionally, for the same TBAB concentration, the incipient pressure and temperature required for nucleation and re-nucleation of semiclathrate hydrates increase, while the time required for re-nucleation decreases. This study, in general, indicates that with the increase of TBAB concentration in the system, it does help to form semiclathrate hydrates at an early stage.

Conclusions

The experimental study on the phase behavior of semiclathrate hydrate of carbon dioxide in TBAB aqueous solution with a small amount of surfactant for 5, 10, and 20 wt.% TBAB are discussed. The data on phase equilibria of semiclathrate hydrates for 5 and 10 wt.%

Table 3 Temperature and pressure variation with time during the memory effect phenomenon

Number	TBAB (wt.%)	*P* and *T* condition at first run			*P* and *T* condition at re-nucleation (memory effect)		
		T_1^a (K)	P_1^a (MPa)	t_1^a (s)	T_2^b (K)	P_2^b (MPa)	t_2^b (s)
1	5	275.5	1.97	510	277.05	2.06	450
2	10	276.65	1.88	420	278.57	1.97	300
3	20	277.15	1.87	330	279.85	1.89	240

P, pressure; *T*, temperature. [a]T_1, P_1, t_1 = incipient temperature, pressure, and time at nucleation of semiclathrate hydrates (at point C in Figure 6); [b]T_2, P_2, t_2 = incipient temperature, pressure, and time at nucleation of semiclathrate hydrates (at point C′ in Figure 6).

TBAB are in good agreement with the published data from the open literature. The presence of the surfactant, SDS, did not influence the equilibrium conditions for the semiclathrate hydrate system. The memory effect phenomenon is studied for few cases of TBAB concentration. The increase in the concentration of TBAB in the system helps to reduce the time required for re-nucleation of semiclathrate hydrates. Additionally, for the same TBAB concentration, the incipient pressure and temperature required for nucleation and re-nucleation of semiclathrate hydrates increase, while the time required for re-nucleation decreases.

Competing interests
The authors declare that they have no competing interests.

Authors' contributions
AJ developed the experimental setup and carried out the experimental studies. JSS initiated, guided and supervised the work, and drafted the manuscript. NAS and KD carried out validation studies and helped in literature search. All authors read and approved the final manuscript.

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AJ is currently working as a field engineer in Schlumberger. He finished his M.Tech. in Petroleum Engineering from Indian Institute of Technology Madras (IITM). JSS is working as an assistant professor at IIT Madras. His areas of research interest are in gas hydrates, flow assurance, and enhanced oil recovery. NAS is a student at Anna University and is also a lecturer at the University of Baghdad, Iraq. KD is a project officer working at IIT Madras and is under the M. Tech. program in Chemical Engineering in IIT Madras.

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